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NEW POLYORGANOSILOXANES PREPARED FROM MINERAL SILICATES

2nd Annual Report

By

B.R. CURRELL

September 1976

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We have also extended our programme of work on the reactions of polyorganosiloxanes with two main aims; firstly, to increase the molecular weight of the products, and secondly, to produce functionally substituted products. The reactive intermediates that have been used include dimethyldichlorosilane, trichlorovinylsilane, and dichloromethyl-vinylsilane. The reaction of elemental sodium and of a phosphorus ester with the polyorganosiloxane has also been accomplished.

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ABSTRACT

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vinylsilane. The reaction of elemental sodium and of a phosphorus ester
with the polyorganosiloxane has also been accomplished. Future work
will concentrate on optimising the yield from these reactions together
with further chemical modifications of the products obtained.

1. INTRODUCTION

Since our last Annual Report the following objectives have been accomplished:

1.1   the semi-quantitative determination of the structure of the polyorganosiloxane homologues produced by the trimethyl-silylation of the mineral biotite;

1.2   the formulation of a mechanism for the production of higher molecular weight analogues by heat treatment;

1.3   a method for the control of the number of hydroxyl groups bonded to the siloxane backbone;

1.4   the controlled reaction of these hydroxyl groups with a variety of intermediates to produce novel polyorganosiloxanes with potential   industrial use;

1.5   the investigation into the mineral structure as the trimethylsilylation reaction proceeds.

As Currell et al[1] had previously demonstrated the trimethylsilylation reaction of minerals gives novel polyorganosiloxanes. We have identified in greater detail the products of the reaction of biotite. The resultant polymer ($\bar{M}_n \sim 900$) consists of 47% tetrakistrimethylsiloxysilane and 6% hexakistrimethylsiloxydisiloxane, the remainder consists of straight chain and cyclic homologues. These high molecular weight products of varying percentage hydroxyl content are in the molecular weight range up to 2000.

The heat treatment of the initial polyorganosiloxane commences with the straightforward evaporation of the low molecular weight materials. As soon as the temperature is increased above $100^{\circ}C$, there is an increase in the percentage of hydroxylated polyorganosiloxane. The use of infra-red spectroscopy has enabled us to heat control the hydroxyl content of the polymers. If the heat treatment is continued beyond $180^{\circ}C$ recombination of hydroxyl groups and addition polymerisation occurs to give higher molecular weight species

$$\text{\small\textapprox}Si - OH \ + \ HO - Si\text{\small\textapprox} \ \longrightarrow \ \text{\small\textapprox}Si - O - Si\text{\small\textapprox}$$
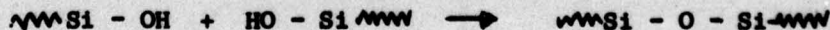
This results in the production of polyorganosiloxanes of ($\bar{M}_n \sim 4000$) with maximum molecular weights estimated to be in the range 7000 - 8000.

The reactions of the hydroxylated polymer with species such as dimethyldichlorosilane and methylvinylchlorosilane at $20^{\circ}C$ has shown that these hydroxyl groups are labile. We are at present

optimising conditions for the reaction of further species such as vinyltrichlorosilane; although this does react at 20 $^{\circ}$C we feel increased yields will result from suitable solvent choice and temperatures.

In our attempts to produce materials in the gap between silicone oils and silicate materials, we have reacted our polyorganosiloxanes with sodium ethoxide and sodium. We have found that sodium produces an intermediate soluble in water which on acidification gives a mixture of silicic acids, the intermediate is almost certainly a sodium salt of the silicic acid. The milder reaction conditions in the sodium ethoxide reaction gave less breakdown and the product was a white solid material which coated the reaction vessel with a thin film. The proposed reaction scheme for these reactions includes products of the type shown below, a form of ionomer

$$\text{—WW— Si - O - } \underset{\underset{OSi(CH_3)_3}{|}}{\overset{\overset{OSi(CH_3)_3}{|}}{Si}} \text{ - O}^{-}\text{---Na}^{+}$$
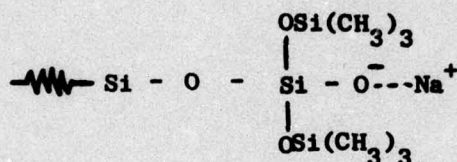
The phosphorus containing additives that have been reacted also add onto the siloxane backbone, although some reorganisation of the backbone occurs. The evidence suggests that the phosphorus materials are bonded onto the higher molecular weight species and obviously these materials (as shown below) may be useful in the lubricants field.

$$\text{—WW— Si - O - P} \overset{Ph}{\underset{Cl}{<}} \qquad \text{—WW— Si - O - } \overset{\overset{O}{\|}}{P} \overset{Cl}{\underset{Ph}{<}}$$
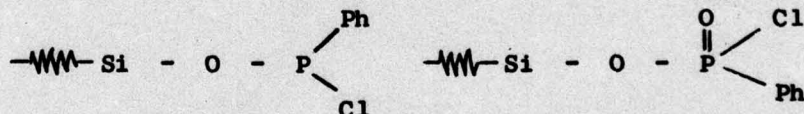
Finally, in this preliminary survey of our years achievements, the trimethylsilylation reaction is continuing to give us greater insights into mineral structures; more so than the original work by Lentz suggested. Even after very long reaction times, both the biotite and phlogopite remaining after reaction are identical to the starting mineral - there is some slight movement of potassium ions in phlogopite, but even this small change does not occur with biotite. This implies that preferential leaching of certain cations does not occur and that reaction of specific parts of the backbone are not kinetically favoured. The high yield of the low molecular weight analogues seems to suggest that the backbone aluminium exists in domains and not as many authors would predict in a regular array.

2.   DISCUSSION

2.1   Introduction

The initial product of the trimethylsilylation reaction
of the mineral biotite is a complex mixture of cyclic
and straight chain siloxanes with some of the trimethyl-
siloxy sites occupied with an hydroxyl group. Reactions
of the crude polyorganosiloxane with phenyl isocyanate,
thionyl chloride and diphenylchlorophosphine gave
interesting materials, but it was difficult to purify and
separate the mixture of products. In order to optimise
the yields of novel polyorganosiloxane prepared by this
method, two lines of investigation have been followed.
Firstly, the structure of the initial polyorganosiloxane
has been fully investigated, and this polymeric material
can be pre-treated before further reactions are attempted.
Secondly, instead of reacting "carbon" based low molecular
intermediate reactants, silicon based materials e.g.
trichlorovinylsilane, dichlorodivinylsilane, dichloro-
methylvinylsilane, are now being used. Literature
evidence suggests that the order of reactivity of an
organosiliconchloride compound with silanol is in the
order trichloro $>$ dichloro $>$ monochloro, although all of
these species should be more reactive than the chlorine
compounds we have previously attempted to react in this
system. These reaction products will be of intermediate
molecular weight but it will be possible to form cross-
links through the functional organic groups thereby
considerably increasing the molecular weight of the
products.

2.2   The Action of Heat on the polyorganosiloxanes

The physical characteristics of the polyorganosiloxanes
produced by the trimethylsilylation of the mineral biotite
can be altered by heat treatment. After separating the
initial polyorganosiloxane product from the aqueous phase,
unreacted mineral and the hexamethyldisiloxane/isopropyl
alcohol mixture its molecular weight was determined
($\bar{M}_n \sim 900$, vapour phase osmometry in benzene). This

product is independent of the time scale of the experiment, however increased yields of the polyorganosiloxane result from increased reaction times, and decreased mineral particle size. On heating this material under a variety of conditions various products are obtained which are shown in table 1. The variation of $\bar{M}_n$ (the number average molecular weight) with temperature is shown in figure 1. This simply shows that any increase in temperature will increase the number average molecular weight. The effect of altering the pressure is shown in figure 2. The polymeric product was heated for five hours at 3 mm, 150 mm and 760 mmHg respectively and as the pressure was decreased the molecular weight increased. This is synonymous with the observed temperature effect. An explanation of these observations is that the low molecular weight homologues tetrakistrimethylsiloxysilane (b.p. 228 $^\circ$C) (I) and hexakistrimethylsiloxydisiloxane (b.p. 303 $^\circ$C) (II), are being driven off by heat, the results of measuring the loss of the two homologues by gas liquid chromatography is shown in figure 3. If the siloxane is heated for five hours at various temperatures up to 1000 $^\circ$C the weight losses shown are observed; the curve begins to plateau at 250 $^\circ$C with a weight loss of about 65%.

The relative weight loss of tetrakistrimethylsiloxysilane (I) follows the overall weight loss curve so that at about 200 $^\circ$C, at both atmospheric and 3 mmHg pressure it has been completely removed. The other volatile component (II) remains with the high molecular weight material until harsher treatment is used.

The starting polymer ($\bar{M}_n$ = 890) was analysed for I and II; these two components were separated using preparative gas liquid chromatography apparatus. Using the technique of standard addition, the percentages of I and II in the original sample were calculated as 47% and 6% respectively. The definition of the number average molecular weight,

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$ (where M_i is the molecular weight of the

The variation of $\bar{M}_n$ (vapour phase osmometry) with temperature for polyorganosiloxanes

⊙ 3 mm Hg
✕ 760 mm Hg
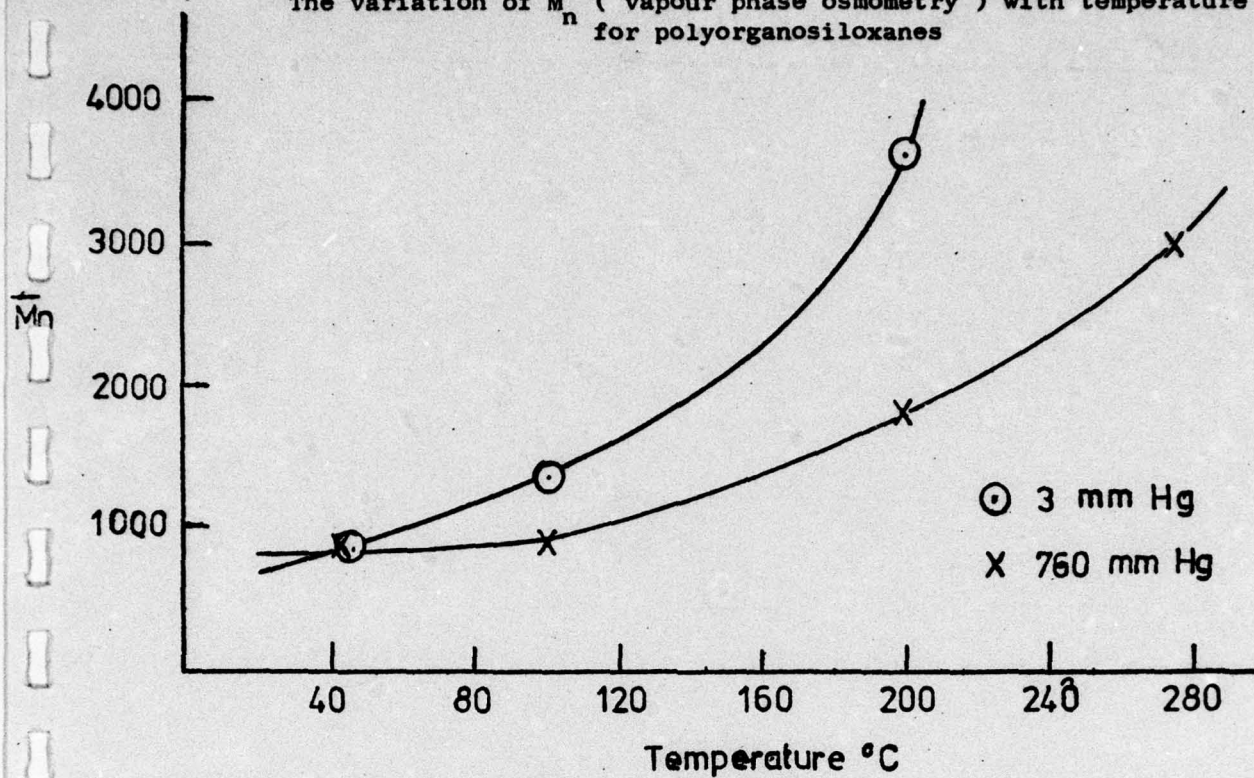
Temperature °C

Fig 1.

The variation of $\bar{M}_n$ with pressure on heating at 100°C for 5 hours

(mm Hg)

Fig 2.

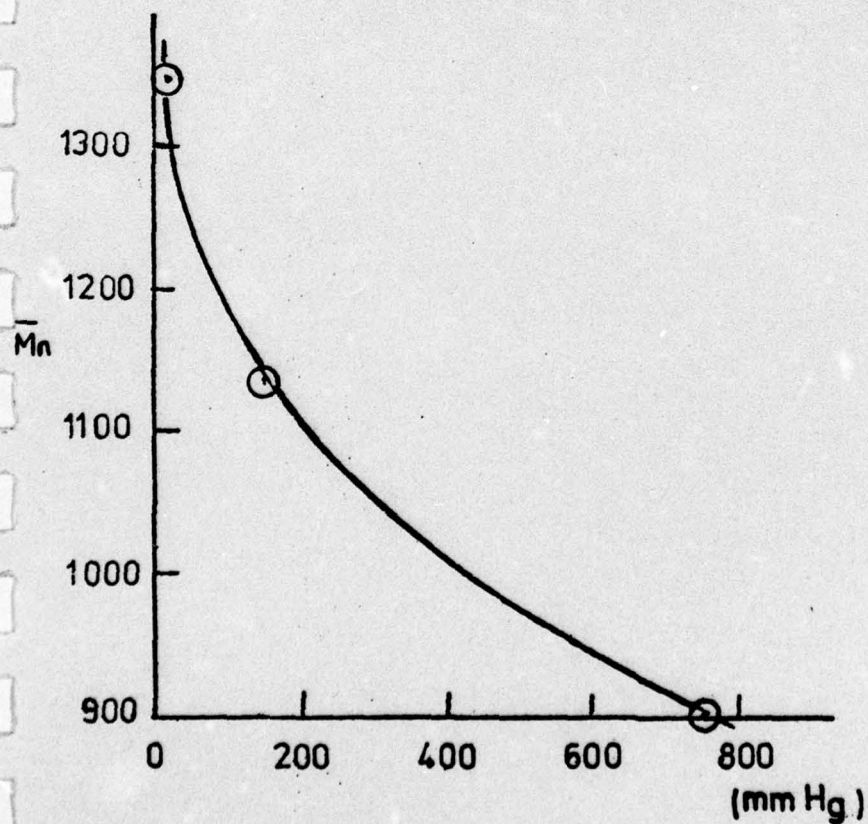**Variation of the weight loss of low molecular weight homologues with temperature**
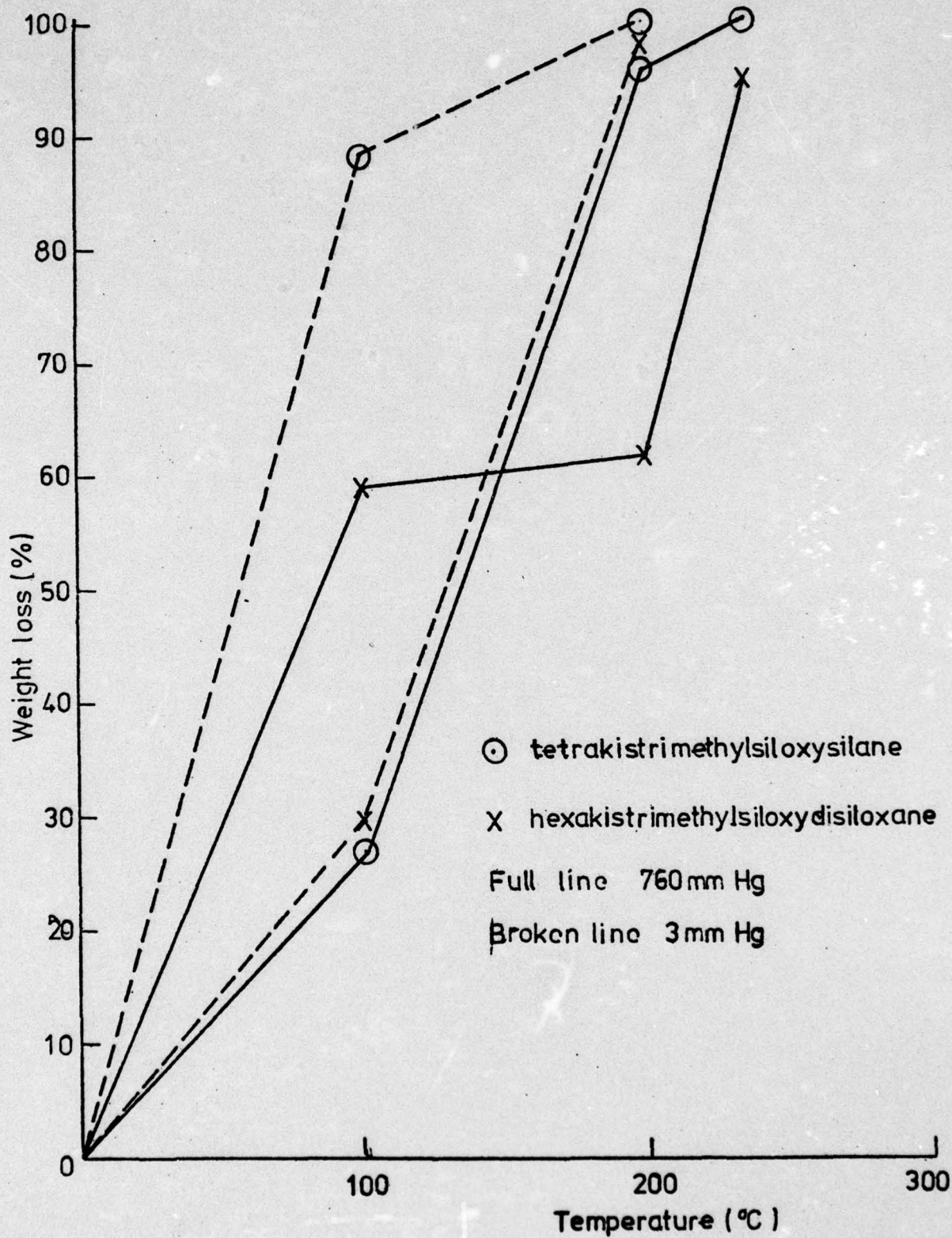

Fig 3.

Variation of weight loss of biotite polymer with temperature
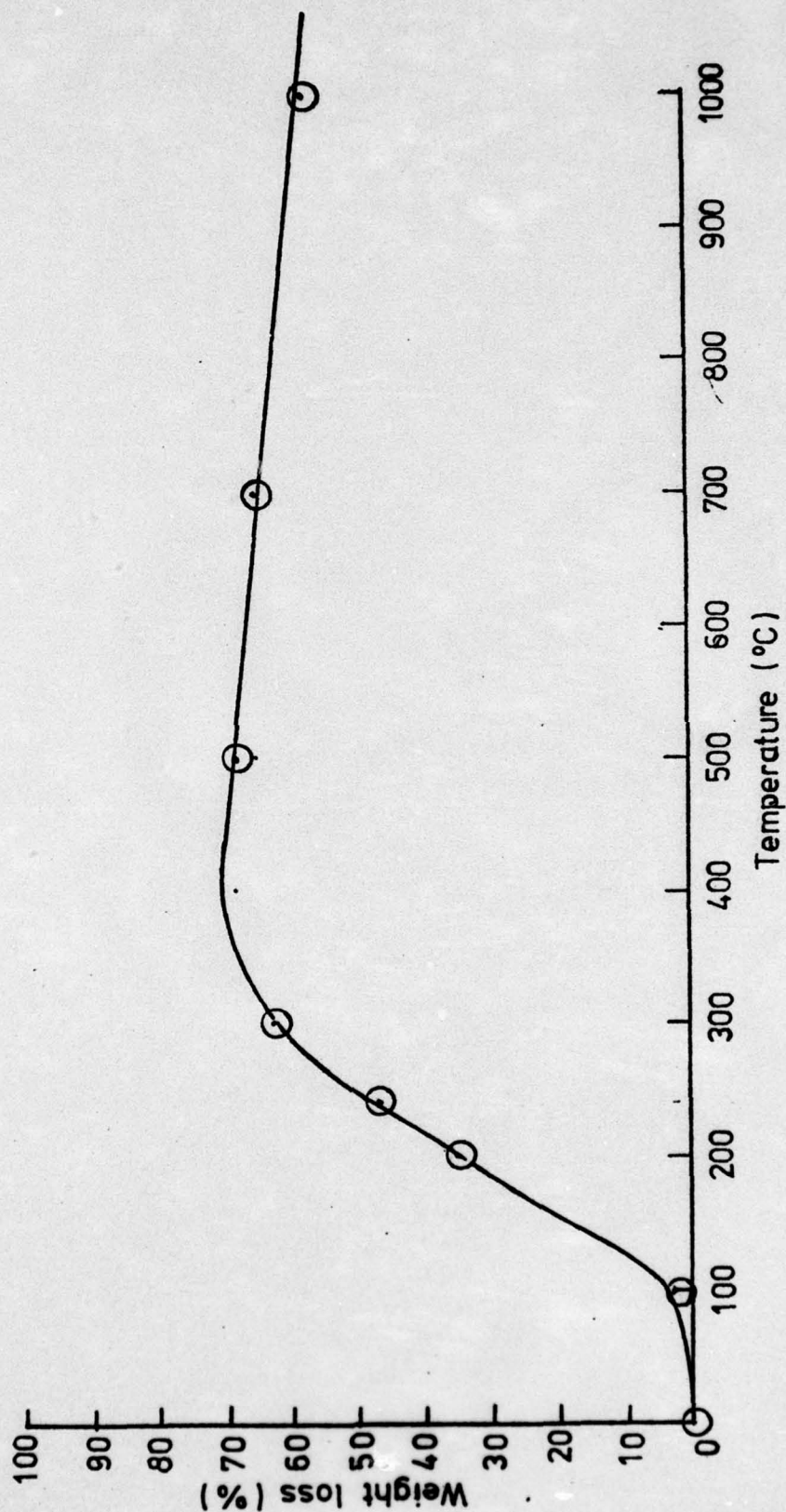over five hour time period at atmospheric pressure

Fig 4.

ith component, and N_i the number of molecules of the ith component present) together with the percentage composition of I, and II present allows us to make a semi-quantitative analysis of the polymers. It also allows us to demonstrate that the effect of heat on the polymer causes some poly-merisation as well as simple removal of I and II. The definition of M_n may be expanded,

$$M_n = \frac{\sum N_i M_i}{\sum N_i} = \sum \frac{N_i}{\sum N_i} \ M_i = \sum x_i M_i$$

where x_i is the mole fraction of the ith component.

Hence for the starting polymer the polymer can be expressed as

$$890 = 0.47 \times 384 + 0.06 \times 606 + 0.47 \ M_{n_x}$$

where M_{n_x} is a parameter which describes the nature of the higher molecular weight analogues, M_{n_x} has a value of 1432. Where the polymer is heated for five hours at atmospheric pressure, the weight loss of 2.5% is represented by weight loss in I and II, we can thus calculate the number average molecular weight as follows :

$$M_{n_{theor}} = 0.35 \times 384 + 0.02 \times 606 + 0.63 \times 1432$$
$$= 1058$$

This figure is close enough to the observed value ($M_{n_{obs}} = 901$) to illustrate that little or no polymerisation has occurred. If this analysis is repeated for further heating experiments, the calculated values begin to show marked differences from the observed values, at 200 $^{\circ}$C/5 hrs., $M_{n_{theor}}$ 1394, $M_{n_{obs}}$ 1789. This analysis seems to indicate that little or no polymerisation occurs below 100 $^{\circ}$C at atmospheric pressure and even at pressures of 3 mmHg little polymerisation occurs.

It would appear that at temperatures greater than 180 $^{\circ}$C that polymerisation occurs caused by condensation of hydroxyl groups, this agrees with the infrared evidence

obtained. Up to about 150 $^{\circ}$C the main result from the
heat treatment is straightforward removal of lower
molecular weight analogues.

The empirical formula for the straight chain trimethyl-
silylated species produced in these reactions can be
written as 222n + 162, where n is the number of Si-O
units in the backbone. If we assume an even distribution
of molecular species excluding tetrakistrimethylsiloxy-
silane and hexakistrimethylsiloxydisiloxane for the
highest molecular weight material we have so far obtained
the maximum chain length of Si-O units is 32, molecular
weight $\sim$7300.

2.3 The reactions of the polyorganosiloxanes

The two main purposes in the reactions described below are
firstly, to increase the molecular weight of the poly-
organosiloxane produced by the trimethylsilylation reaction
and secondly, to transform the polyorganosiloxane into a
reactive intermediate which itself may be a useful novel
polyorganosiloxane. But more important than this
will be the possibility to modify these products under
controlled conditions. Our overall aim is, therefore, to
produce materials to fill the gulf between mineral silicates
on the one hand, and silicone fluids on the other.

2.3.1. Acid polymerisation

The nature of the phase equilibrium established between
hydrochloric acid, water, isopropanol and hexamethyldisiloxane
may allow a small amount of residual hydrochloric acid to be
present with the polyorganosiloxane even after carrying out
careful separation procedures. This may result in acid
catalysed condensation reactions, or the production of
hydroxyl groups by exchange with the trimethylsilyl group.

$$\text{-\!\!\bigwedge\!\!\bigwedge\!\!-SiOX} + \text{HCl} \longrightarrow \text{-\!\!\bigwedge\!\!\bigwedge\!\!-SiOH} + \text{XCl}$$
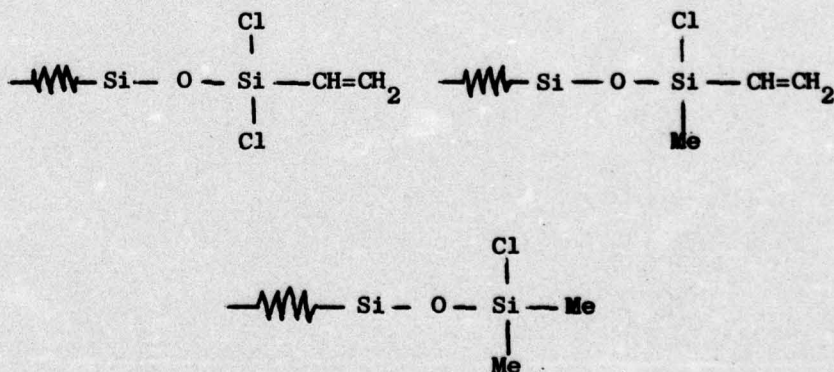
$$X = SiMe_3$$
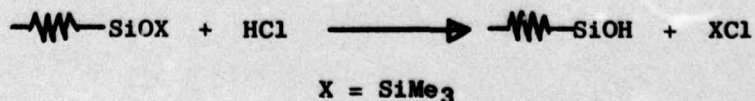
However two polymers produced by identical procedures, except one was treated during the isolation procedure with sodium bicarbonate to remove acid, gave spectroscopically identical polymers with identical molecular weights ($\bar{M}_n$ 2041 and 2045 respectively).

The ratio of hydrochloric acid to polymer was increased to 1:1 in a further experiment; these two components were stirred for twenty-four hours under nitrogen. The results indicated that little or no polymerisation had occurred even in the presence of an excess of hydrochloric acid.

2.3.2 The reactivity of the hydroxyl group

The hydroxyl group attached to the siloxane backbone is reactive towards the silyl chloride bond. The biotite polyorganosiloxane (M_n 1372) was dissolved in hexamethyl-disiloxane and was stirred with trimethylchlorosilane for twenty-four hours at ambient temperatures. The hydroxyl groups detected by infrared spectroscopy on the starting material were absent in the product. The increase in molecular weight, in this experiment (M_n 1593) suggested that three hydroxyl groups per molecule had been replaced. Preliminary experiments using further silyl chloride species have shown that this reaction may generally be applicable and the formation of species such as those shown below will occur.

$$-\!\!\!\bigwedge\!\!\!\bigwedge\!\!\!\bigwedge\!- \overset{}{Si} - O - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{Si}} - CH\!=\!CH_2 \qquad -\!\!\!\bigwedge\!\!\!\bigwedge\!\!\!\bigwedge\!- \overset{}{Si} - O - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Me}{|}}{Si}} - CH\!=\!CH_2$$

$$-\!\!\!\bigwedge\!\!\!\bigwedge\!\!\!\bigwedge\!- \overset{}{Si} - O - \overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Me}{|}}{Si}} - Me$$

These reactions have only been carried out at ambient temperatures, and further work is needed to optimise the yield of the products.

2.3.3 Further reactions.

The biotite polymer has been successfully reacted with
sodium, sodium ethoxide and phosphorus esters. The
products are interesting materials although chemically
difficult to analyse. These reactions have so far been
carried out on a small scale, and current work consists
of operating on at least a 10g scale. The phosphorus
compounds add onto the high molecular weight polyorgano-
siloxane species and can quite easily be identified by
U.V. analysis of the high pressure liquid chromatography
traces. Spectroscopic evidence suggests the formation of
Si-OP bonds on materials of molecular weights of between
35,000 and 110,000 on the polystyrene scale. The reaction
of cations with the polyorganosiloxanes give a white
insoluble species which appear to coat glass in a monolayer.
The reaction of sodium ethoxide with the biotite polymer
again appear to give a reaction which markedly increases
the molecular weight of the original polymer.

2.4. The relationship between the silicate structure and the polyorganosiloxane produced by trimethylsilylation.

The polymer produced by the trimethylsilylation of the
mineral phlogopite indicated that the yield of polymer
produced was directly proportional to the weight of
aluminium leached from the mineral. However, as the
unreacted mineral was found to be identical in chemical
composition, and almost completely identical in chemical
structure, with the starting mineral it seems unlikely
that preferential leaching of any specific cation, and
reaction of a specific part of the mineral backbone is
occurring. The unreacted mineral does have a larger
average particle size ($>3\mu$) compared with the starting
mineral ($<\frac{1}{2}\mu$) which seems to indicate that reaction
depends on particle size. In the case of phlogopite
slight shift of the potassium ions relative to the rest
of the crystal lattice was observed which may be due to
a slight opening of the silicate sheets during reaction.

In an attempt to further clarify the role of aluminium in these reactions a series of reactions were carried out on some model compounds, calcium aluminosilicate glasses with controlled amounts of aluminium present, and the results of the reactions are shown in table 4. The yield of polymer produced is not directly proportional to the percentage of silicon dioxide present, but it seems that there is a critical value of 0.5 for $\dfrac{SiO_2}{Al_2O_3 + CaO}$ ratio

for the maximum yield of polymer. It does appear that there is a relationship between the percentage of tetrakistrimethylsiloxysilane (I) produced and the percentage aluminium present. There is, therefore, some scope for predicting the position of atoms such as aluminium, which have replaced a silicon atom in a sheet silicate structure by analysing the trimethylsilylated products. This method may help to solve the difficult problem of analysing minerals where isomorphous replacement of silicon has occurred.

3. **EXPERIMENTAL**

General Methods of Analysis

3.1   Analytical Methods

(i)   Microanalyses for the elements carbon and hydrogen were
carried out either at the School of Chemistry, Thames Polytechnic,
London, or by the School of Chemistry, Polytechnic of North London
Holloway Road, London.   At Thames Polytechnic analyses were
carried out using a Hewlett Packard Model 185 carbon, hydrogen and
nitrogen analyser.

(ii)   Differential thermal analyses were recorded using a
Standata 6 - 25 Differential Thermal Analyser. The samples
were heated in an atmosphere of air using alumina as a standard.
The furnace was programmed to give a linear increase in temperature
from ambient to $1000^{\circ}C$ over a period of approximately 2 hours.

(iii)   Differential scanning calorimetry was performed on certain
products using a Perkin Elmer DSC-2. The instrument was programmed
to give a temperature increase from $270^{\circ}C$ to $773^{\circ}C$ at a rate of
20 deg C min^{-1}.

(iv)   Gel permeation chromatography on the products was performed
either at Thames Polytechnic or at the Rubber and Plastics
Research Association of Great Britain (R.A.P.R.A.). The instrument
used at Thames Polytechnic was a Waters Associates Model 501, High
Performance Liquid Chromatograph comprising four μ-Styragel
columns with permeability ranges 100 $\overset{o}{A}$, 500 $\overset{o}{A}$, 10^3 $\overset{o}{A}$ and 10^4 $\overset{o}{A}$,
each having a plate count of greater that 3000. Peaks were
detected in both cases using refractive index detectors and
relative molecular weights assigned by calibrating the instruments
with Waters Associates polystyrene and polyglycol standards. The
eluting solvents used were chloroform at Thames Polytechnic
and tetrahydrofuran and o-dichlorobenzene at R.A.P.R.A.

(v)   A modified Zerewitinoff method[2] was used to determine hydroxyl
groups present on the polymers. The Grignard reagent was prepared
by the method of Siggia[3] and the apparatus calibrated using phenol
and β-naphthol.

(vi)   The products from the polyorganosiloxane derivatives (2µl) were dissolved in chloroform and applied to a glass plate coated with silica gel.   The plate was run in a tank containing benzene/ethyl acetate and developed with iodine vapour. The method of Hoebbel[4]   has been investigated as a further thin layer chromatography method.

Physical Methods

(i)   Infrared spectra were recorded using a Perkin Elmer Model 337 Grating Infrared Spectrophotometer over the wavelength range 4000 - 400 cm^{-1}. All greases and liquids were examined as capillary films between either potassium bromide or sodium chloride plates; starting and unreacted minerals from trimethylsilylation reactions were run as potassium bromide discs; and low melting solids were run by pressing between two potassium bromide plates, or by deposition from ether.

(ii)   Molecular weights were determined using a Knauer vapour pressure osmometer.   The instrument was calibrated using solutions of benzil, polystyrene and polyglycols in chloroform.

(iii)   Gas Liquid Chromatographic analyses were carried out using a *Pye Series* 104 Gas Chromatograph. The methods of Gotz and Masson[5] and Lentz[6] were used to identify the compositions of reaction products from trimethyl silylation of mineral silicates.

(iv)   Nuclear magnetic resonance spectra were recorded using a Varian A-60A 60 MHz spectrophotometer.   The instrument was used exclusively for examining reaction products for the presence of hydroxyl groups remaining on the siloxane backbone of the polymers after the trimethylsilylation reaction.

(v)   X-ray powder diffraction.
The photograph was taken on a Enraf Nonius TN20 X-ray diffractometer using a copper target and a nickel filter at 30Kv, 18 mA. The 180mm film was exposed for 10 hours.

(vi)   Atomic Absorption spectroscopy
This work was carried out on a Varian Techtron AA6 atomic absorption spectrophotometer.

3.2   The Action of Heat on the Polymers

The polymeric material produced by the trimethylsilylation of
the mineral biotite was heated under different conditions.
The polymer was heated under varied conditions of temperature,
pressure, and for different lengths of time. In a typical
reaction the polymer (2.86g) (Found: C, 30.96%; H, 8.12%;
$\overline{Mn}$ 890), was heated in a drying pistol (200 ^{o}C; 760 mmHg)
for 5.0 hours. The product was a viscous liquid (1.85g) weight
loss 35.3% (Found: C, 27.92%; H, 7.68%; $\overline{Mn}$ 1785).   This residue
was analysed by infrared spectroscopy for hydroxyl groups and the
percentage composition of tetrakistrimethylsiloxysilane and hexa-
kistrimethylsiloxydisiloxane present in the material was
calculated by gas liquid chromatography. This enabled the original
composition of the original polymer to be established semi-quantitatively.

3.3   The Reaction of the polymers with low molecular weight species

3.3.1 Purification of solvents

(a)   Hexamethyldisiloxane

Hexamethyldisiloxane (G.P.R. grade) was distilled prior to use
(bp   99.0 - 99.5 ^{o}C; lit. bp 100.4 ^{o}C).[7]

(b)   Carbon tetrachloride

Carbon tetrachloride (G.P.R. grade) was dried for 1 day over
molecular seive (type 4A).

(c)   Di-n-butyl ether

Di-n-butyl ether (G.P.R. grade) was passed down a column of
activated alumina to remove peroxides and then distilled over
a mixture of calcium hydride and sodium (bp 138 - 141 ^{o}C; lit. bp 142.2
^{o}C).[8]

(d)   Ethanol

Ethanol (G.P.R. grade) was used as supplied.

3.3.2 General method for reacting polymers

Biotite polymer, characterised by elemental analyses for carbon
and hydrogen and molecular weight measurement by vapour pressure
osmometry, was dissolved in an appropriate solvent. The reagent in solvent
was added to the polymer and the mixture stirred under nitrogen
at 20 ^{o}C for 4 hours.

The solvent and excess reagent were removed under reduced pressure and the product dried to constant weight in a drying pistol (45 $^{\circ}$C, 3mmHg). A summary of reaction conditions, elemental analysis for carbon and hydrogen and molecular weight determinations for the products are to be found in tables 2 and 3.

3.2.1 Reaction with sodium ethoxide

Biotite polymer (0.501g, 0.00025 mole) (Found: C, 28.71%; H, 7.33%; M̄n 1981) was dispersed in ethanol (10 cm^3). Sodium metal (0.504 g, 0.022 mole) was dissolved in ethanol (15 cm^3) to give sodium ethoxide (1.490g) and this was added to the polymeric dispersion. The mixture was refluxed (78 $^{\circ}$C) under nitrogen for 4 hours. After the mixture was allowed to cool and water (30 cm^3) added. The polymeric material was extracted with chloroform (4 x 10 cm^3) and dried over molecular seive (type 4A). The solvent was removed and the polymeric material dried to constant weight (45°, 3 mmHg) to give the product (0.034 g).

The molecular seive material used to dry the chloroform layer was extracted with ether, the solvent removed and the residue redissolved in chloroform. The major peak by high performance liquid chromatography was between 110,000 and 35,000 molecular weight on the polystyrene scale.

3.3.2 Reaction with molten sodium

Sodium (0.488g, 0.021 mole) was dispersed in the form of small globules in di-n-butyl ether (35 cm^3) under nitrogen. Biotite polymer (0.493g, 0.00025 mole) was dissolved in di-n-butyl ether (15 cm^3) and added to the sodium. The mixture was refluxed (140 $^{\circ}$C) for 4 hours. After cooling ethanol (30 cm^3) was added followed by water (40 cm^3) and the mixture allowed to separate. The aqueous ethanol layer was run off and extracted with more di-n-butyl ether. The ether extracts were combined and dried over molecular seive (type 4A). The solvent was removed under reduced pressure and the polymeric material dried to constant weight (55 $^{\circ}$C, 1.5 mmHg) to give the product (0.0817g).

3.3.3 Reaction with hydrochloric acid

Biotite polymer (1.003g, 0.0010 mole)(Found: C, 31.91%;H, 8.15%; Mn, 985) was refluxed (76 ^{o}C) with concentrated hydrochloric acid (0.526g, 0.014 mole), (d= 1.18), in dry carbon tetrachloride (20 cm^3) under nitrogen for 24 hours. The solution of product in carbon tetrachloride was washed with sodium bicarbonate solution (10%, 5 x 10 cm^3) and dried over molecular seive (type 4A). Solvent was removed under reduced pressure and the polymeric material dried to constant weight (45 ^{o}C, 3 mmHg) to give the product (0.709g), (Found: C, 30.52%; H, 8.22%; Mn, 814). A blank was performed, (Found: C, 31.08%; H, 8.24%; Mn, 792).

3.3.4 The trimethylsilylation reactions of calcium aluminosilicate glasses.

In a typical reaction a sample of a glass 191ALD (composition: SiO_2 36.9%; Al_2O_3 26.8%; CaO 36.3%) was trimethylsilylated using the previously described mixture of hydrochloric acid, isopropanol, hexamethyldisiloxane and water. The polymeric product was isolated and analysed by glc to give the following percentages of tetrakistrimethylsiloxysilane,[I] hexakistrimethyl-siloxydisiloxane[II], octakistrimethylsiloxytrisiloxane[III] and decakistrimethylsiloxytetrasiloxane[IV]. (Found : I, 58.8%; II, 26.9%; III, 13.4%; IV, 0.9%). The results for the other glasses are shown in table 4. We acknowledge the gift of four glass materials from Corning Glass.

D.   TABLES OF DATA

Table 1

Polymers prepared from the mineral biotite

Treatment Temp ($^{\circ}$C)	Pres. (mmHg)	Time (Hrs)	Wt.loss %	$\bar{M}_n$	Carbon (%)	Hydrogen (%)	$\dagger$ % I lost	% II lost
45	3	5	-	890	30.96	8.12	0.0	0.0
100	3	5	21.0	1342	29.35	7.86	88.1	29.9
100	150	5	28.7	1130	29.93	7.82	36.8	23.9
200	3	5	67.5	3556*	26.00	6.87	100.0	98.1
200	3	10	59.7	4128			100.0	100.0
100	760	5	2.5	901	30.75	8.07	27.0	59.1
200	760	5	35.3	1785	27.92	7.67	96.4	61.0
235	760	5	47.0	2981	25.85	6.65	99.7	94.8
300	760	5	62.6	- $\ddagger$	3.52	1.71	-	-
315	760	0.5	32.7	1029	30.64	7.69	78.2	72.5
500	760	5	68.0	- $\ddagger$	0.00	0.00	-	-
700	760	5	66.0	- $\ddagger$	0.00	0.00	-	-
1000	760	5	57.5	- $\ddagger$	0.00	0.00	-	-

I   tetrakistrimethylsiloxysilane

II   hexakistrimethylsiloxydisiloxane

$\dagger$ based on 100% I, II   originally

$\ddagger$ insoluble products

* melting point range 108 - 145°C

Table 2

Reaction conditions for the polymers derived
from the mineral biotite

Wt of polymer (g)	Molarity polymer	Reactant (g)	Molarity reactant	Solvent (cm^3)	Temp ($^\circ$C)	Time (HR)	Drying Conditions ($^\circ$C, mmHg)
0.728	0.00052	BzCl (7.300)	0.058	*HMD (20)	20	24	65, 1.5
0.973	0.00049	Cl_2Me_2Si (10.877)	0.084	CCl_4 (50)	20	4	45, 3
0.981	0.00050	$Cl_2MeViSi$ (9.947)	0.071	CCl_4 (50)	20	4	45, 3
1.014	0.00051	Cl_3ViSi (10.431)	0.065	CCl_4 (50)	20	4	45, 3
†0.532	0.00027	$PhPOCl_2$ (0.549)	0.0028	CCl_4 (30)	20	4	-

* Hexamethyldisiloxane

† Sample not dried injected in solution into hplc.

Table 3

Elemental analysis and molecular weights of
starting materials and products

	Polymer				Reactant	Product			
	Wt taken (g)	C %	H %	Mn		Wt(g)	C %	H %	Mn
Biotite	0.728	29.36	7.57	1406	BzCl	0.332	27.84	7.49	2396
Blank	–	29.36	7.57	1406	–	–	28.28	7.58	1623
Biotite	0.973	28.71	7.33	1981	Cl_2Me_2Si	0.973	28.64	7.22	1941
Biotite	0.981	28.71	7.33	1981	$Cl_2MeViSi$	0.920	28.32	7.22	1659
Biotite	1.014	28.71	7.33	1981	Cl_3ViSi	0.873	28.64	7.06	2059
Blank	–	28.71	7.33	1981	–	–	–	–	1711

Table 4

The trimethylsilylation of some calcium aluminosilicates

Glass	Glass Composition %			Polymer	Analysis of products (%)[†]			
Code No.	SiO_2	Al_2O_3	CaO	Yield (%)	I	II	III	IV
191 ALD	36.9	26.8	36.3	89.1	58.8	26.9	13.4	0.9
191 BVJ	6.1	46.2	47.7	10.1	86.6	10.2	3.2	0.0
191 CGS	64.0	9.1	26.0	1.5	92.2	6.5	1.3	0.0
191 CDN	90.0	5.0	5.0	0.9	30.2	43.7	24.4	1.8

[†] Internal normalisation

5. **FUTURE PROGRAMME**

The future programme of work can be classified under three main headings :

(i)   further investigations will be carried out on the reactivity of the hydroxyl groups bound to the silicate backbone. The addition of functional groups such as vinyl and halogen will lead to secondary reactions, such as epoxidation and halogen substitution.

(ii) a new series of polyorganosiloxanes will be produced by replacing the silylating agent, hexamethyldisiloxane, with, in the first instance, a series of polydimethylsiloxanes. Further species such as $C = C-Si(CH_3)_2-O-Si-(CH_3)_2-C = C$ may also be added. We are also investigating the copolymerisation of the hydrolysis products of dimethyldichlorosilane with the polyorganosiloxane materials.

(iii) the work has now yielded enough results for a structural analysis on the position of aluminium atoms which have replaced silicon in the sheet silicate, further work will be attempted in this area.

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<u>Annex</u> - DA-ERO-75-G-019:- 1st October 1975 - 30th September 1976.

(a)   There are no unused funds remaining on the contract as at the
        30th September 1976.

(b)   No property has been acquired at direct contract expense during
        this period.